#7/4-7-03
28 FC

OIPE JC104
MAR 1 2 2003
PATENT & TRADEMARK OFFICE

Docket No.: 43890-427

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RECEIVED
MAR 17 2003
TECHNOLOGY CENTER 2800

In re Application of	:	
	:	
Kazuyo SAITO et al.	:	
	:	
Serial No.: 09/616,944	:	Group Art Unit: 2812
	:	
Filed: July 14, 2000	:	Examiner: Ha T Nguyen
	:	

For: ELECTROLYTIC CAPACITOR AND ITS MANUFACTURING METHOD

SUBMISSION OF CERTIFIED ENGLISH TRANSLATIONS OF FOREIGN PRIORITY DOCUMENTS

Commissioner for Patents
Washington, DC 20231

Sir:

Enclosed are certified English translations of the Foreign Priority Documents (JP 10-015269, JP 10-350072) for the above-identified application so as to perfect the Applicants' claim of foreign priority.

Respectfully submitted,

MCDERMOTT, WILL & EMERY

for #46,692

Michael E. Fogarty
Registration No. 36,139

600 13th Street, N.W.
Washington, DC 20005-3096
(202) 756-8000 MEF:MWE
Date: March 12, 2003
Facsimile: (202) 756-8087

43890-427

PATENT

OIPE JC105
MAR 12 2003
PATENT & TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Kazuyo Saito et al. : Art Unit
Serial No.: 09/616,944 : Examiner
Filed: July 14, 2000 :
FOR: ELECTROLYTIC CAPACITOR AND ITS MANUFACTURING METHOD

RECEIVED
MAR 17 2003
TECHNOLOGY CENTER 2800

VERIFICATION OF A TRANSLATION

Assistant Commissioner for Patents
Washington, D.C. 20231
SIR :

I, the below named translator, hereby declare that:

2. My name and post office address are as stated below.

3. That I am knowledgeable in the English language and in the language of JPH10-350072, and I believe the attached English translation to be a true and complete translation of JPH10-350072.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

43890-427 PATENT

Date: January 31, 2003

Katsuyuki Hirano

Full name of the Translator

K. Hirano

Signature of the Translator

c/o AIN Co., Ltd., Kyo-oto-Bldg., 3rd Floor, 4-6-12,
Hirano-machi, Chuo-ku, Osaka-shi, Osaka, Japan

Post Office Address

[NAME OF THE DOCUMENT] Patent Application
[ARRANGEMENT NUMBER] 2174000051
[DATE OF FILING] December 9, 1998
[ADDRESS] Director-General of the Patent Office
[INTERNATIONAL PATENT CLASSIFICATION] H01G 9/00
[TITLE OF THE INVENTION] Electrolytic Capacitor
[NUMBER OF CLAIMS] 12

[INVENTORS]
[NAME] Kazuyo SAITO
[ADDRESS] c/o Matsushita Electric Industrial Co., Ltd.
1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
[NAME] Yukihiro NITTA
[ADDRESS] c/o Matsushita Electric Industrial Co., Ltd.
1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
[NAME] Hiroshi TADA
[ADDRESS] c/o Matsushita Electric Industrial Co., Ltd.
1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
[NAME] Shigeyoshi IWAMOTO
[ADDRESS] c/o Matsushita Electric Industrial Co., Ltd.
1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu

[APPLICANT]
[INDENTIFICATION NUMBER] 000005821
[NAME] Matsushita Electric Industrial Co., Ltd.
[ADDRESS] 1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
[POSTAL CODE] 571-8501

[AGENT]
[IDENTIFICATION NUMBER] 100097445
[NAME] Fumio IWAHASHI, Patent Attorney

[ADDRESS] c/o Matsushita Electric Industrial Co., Ltd.
1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
[POSTAL CODE] 571-8501
[SELECTED AGENT]
[IDENTIFICATION NUMBER] 100103355
[NAME] Tomoyasu SAKAGUCHI, Patent Attorney
[ADDRESS] c/o Matsushita Electric Industrial Co., Ltd.
1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
[POSTAL CODE] 571-8501
[SELECTED AGENT]
[IDENTIFICATION NUMBER] 100109667
[NAME] Hiroki NAITO, Patent Attorney
[ADDRESS] c/o Matsushita Electric Industrial Co., Ltd.
1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
[POSTAL CODE] 571-8501

[PRIORITY CLAIMED BASED UPON THE PRIOR APPLICATION]
[APPLICATION NUMBER] H10-015269
[DATE OF FILING] January 28, 1998

[REPRESENTATION OF FEE]
[PAYING METHOD] In-advance payment
[NUMBER IN LEDGER OF IN-ADVANCE PAYMENT] 011305
[AMOUNT] 21000

[LIST OF ARTICLES FILED]
[NAME OF ARTICLE] Specification 1
[NAME OF ARTICLE] Drawing 1
[NAME OF ARTICLE] Abstract 1

[NUMBER OF GENERAL POWER] 9809938

[Name of the Document] Specification

[Title of the Invention] Electrolytic capacitor

[What is claimed is]

[Claim 1] An electrolytic capacitor comprising a capacitor element composed of an anode foil formed of a valve action metal having a dielectric oxide film formed on the surface, a cathode foil, and a solid organic conductive material disposed between said anode foil and cathode foil, a metal case of a tubular form with a bottom for accommodating this capacitor element together with a driving electrolyte solution, and a sealing member for sealing the opening of this metal case.

[Claim 2] An electrolytic capacitor of claim 1, wherein said solid organic conductive material is composed of either an organic semiconductor or a conductive high polymer, or both.

[Claim 3] An electrolytic capacitor of claim 2, wherein said organic semiconductor is composed of 7,7,8,8-tetracyanoquinodimethane complex and its derivative.

[Claim 4] An electrolytic capacitor of claim 2, wherein said conductive high polymer is at least one or more selected from the group consisting of pyrrole, aniline, thiophen, ethylene dioxythiophen, sulfonated aniline, sulfonated pyrrole, sulfonated thiophen, sulfonated ethylene dioxythiophen, and their derivative polymers.

[Claim 5] An electrolytic capacitor of claim 4, wherein said conductive high polymer is at least one or more selected

from the group consisting of liquid phase chemical polymerization composition, vapor phase polymerization composition, liquid phase electrolytic polymerization composition, and residual dry polymer of soluble polymer solution.

[Claim 6] An electrolytic capacitor of claim 4 or 5, wherein said conductive high polymer is at least one or more selected from the group consisting of chemically polymerized polypyrrole, polyethylene dioxythiophen, and polyaniline, electrolytically polymerized polypyrrole, polyethylene dioxythiophen, and polyaniline, and dry residue sulfonated polyaniline obtained by drying soluble polyaniline derivative solution.

[Claim 7] An electrolytic capacitor of any one of claims 1 to 6, wherein said driving electrolyte solution is prepared by dissolving an organic acid salt and an inorganic acid salt in a organic solvent capable of swelling by immersing in a solid organic conductive material.

[Claim 8] An electrolytic capacitor of claim 7, wherein said electrolyte to be dissolved in the driving electrolyte solution has a concentration of 1 wt.% of the base or hydroxide of the base in the base for composing the electrolyte, and a hydrogen ion concentration of 1.0×10^{-13} mol/dm^3 or more in an aqueous solution of the base or hydroxide of the base at the measuring temperature of 30°C.

[Claim 9] An electrolytic capacitor of claim 8, wherein the base for composing said electrolyte is at least one or more selected from the group consisting of a compound having alkyl subsistent amidine group, quaternary salt of compound having alkyl substituent amidine group, tertiary amine, and ammonium.

[Claim 10] An electrolytic capacitor of claim 9, wherein the quaternary salt of compound having alkyl subsistent amidine group is at least one or more selected from the group consisting of imidazole compound, benzoimidazole compound, and alicyclic amidine compound, being rendered quaternary by alkyl group or aryl alkyl group with 1 to 11 carbon atoms.

[Claim 11] An electrolytic capacitor of claim 10, wherein the quaternary salt of compound having alkyl subsistent amidine group is at least one or more selected from the group consisting of 1-methyl-1,8-diazabicyclo [5,4,0] undecene-7, 1-methyl-1,5-diazabicyclo [4,3,0] nonene-5, 1,2,3-trimethyl imidazolinium, 1,2,3,4-tetramethyl imidazolinium, 1,2-dimethyl-3-ethyl-imidazolinium, 1,3,4-trimethyl-2-ethyl imidazolinium, 1,3-dimethyl-2-heptyl imidazolinium, 1,3-dimethyl-2-(-3' heptyl) imidazolinium, 1,3-dimethyl-2-dodecyl imidazolinium, 1,2,3-trimethyl-1,4,5,6-tetrahydropyrimidium, 1,3-dimethyl imidazolium, 1-methyl-3-ethyl-imidazolium, and 1,3-dimethyl benzoimidazolium.

[Claim 12] An electrolytic capacitor of claim 11, wherein the boiling point of the solvent of the driving electrolyte

solution is 200°C or more, the electric conductivity of the driving electrolyte solution at measuring temperature of 30°C is 1.0 mS/cm or more, and the spark ignition voltage is 80 V or more.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an electrolytic capacitor of high dielectric strength excellent in impedance characteristic, leak current characteristic, and reliability, by using both solid organic conductive material and a driving electrolyte solution.

[0002]

[Prior Art]

In the recent trend of electronic appliances becoming digital and higher in frequency, the electrolytic capacitor, one of the electronic components, is required to be larger in capacity than in the conventional part and be superior in impedance characteristic in high frequency region. To meet such demand, it has been attempted to enhance the conductivity of the driving electrolyte solution (hereinafter called electrolyte solution), decrease the resistance of separator, or use a conductive compound obtained by making conductive a sheet insulator such as paper, cloth, nonwoven cloth or high polymer film, as a separator.

[0003]

Also as an attempt to make the separator conductive, various methods have bee proposed, such as kneading or mixing of carbon fibers or particles, and compounding with graphite powder. Moreover, by using monomer such as pyrrole, thiophen or aniline, a method of forming a conductive high polymer on the surface by chemical oxidation and polymerization is disclosed (see Japanese Laid-open Patent No. 64-90517).

[0004]

[Problems to be Solved by the Invention]

In the conventional constitution, however, there was a limit in enhancement of conductivity of electrolyte, and its conductivity is at most about ten to scores of mS/cm at the present, and electrolyte having a sufficient conductivity is not developed yet, and an electrolytic capacitor of an electrolyte having a sufficient impedance characteristic is not obtained so far.

[0005]

On the other hand, for decrease of resistance of separator, it has been attempted to decrease the separator thickness, lower the density, make uniform the pore size, or change from paper to high polymer nonwoven fabric, but due to lack of strength by lowering of density and other problems, a sufficient effect of lowering the resistance is not obtained yet.

[0006]

Further, the separator made conductive by kneading or mixing carbon fibers or particles is not sufficient in the electric conductivity, and it was hard to obtain a separator of low density. When using a separator by compounding graphite powder, there was a problem of increase of shorting due to drop of graphite powder and dispersion into electrolyte.

[0007]

On the other hand, in the method of forming a conductive high polymer on the surface by chemical oxidation and polymerization from monomer of pyrrole, thiophen or aniline, it is difficult to compose an electrolytic capacitor of which rated voltage exceeds 35 V because there is almost no effect of deterioration of dielectric oxide film by oxidizing agent or chemical formation of conductive high polymer (defect repairing capability of dielectric oxide film), or if composed, however, increase of leak current or shorting between anode and cathode may occur during aging process or high temperature test.

[0008]

It is hence an object of the invention to solve such problems of the prior art, and present an electrolytic capacitor of high dielectric strength excellent in impedance characteristic, leak current property and reliability.

[0009]

[Means to Solve the Problems]

To solve the problems, the electrolytic capacitor of the

invention uses a capacitor element composed of an anode foil formed of a valve action metal having a dielectric oxide film formed on the surface, a cathode foil, a solid organic conductive material disposed between the anode foil and cathode foil, and a driving electrolyte solution. According to the invention, an electrolytic capacitor of high dielectric strength excellent in impedance characteristic, leak current characteristic, and reliability can be obtained.

[0010]

[Description of the Preferred Embodiments]

The invention as set forth in claim 1 is an electrolytic capacitor comprising a capacitor element composed of an anode foil formed of a valve action metal having a dielectric oxide film formed on the surface, a cathode foil, and a solid organic conductive material disposed between the anode foil and cathode foil, a metal case of a tubular form with a bottom for accommodating this capacitor element together with an electrolyte solution, and a sealing member for sealing the opening of this metal case. In this constitution, by making use of the high conductivity of the solid organic conductive material, the resistance between the electrodes can be extremely decreased in the conductive portion, and an electrolytic capacitor excellent in impedance characteristic can be obtained easily, and at the same by interposing the electrolyte having the defect repairing capability of the

dielectric oxide film of valve action metal, an electrolytic capacitor of low leak current having a high dielectric voltage can be composed.

[0011]

The invention as set forth in claims 2 and 3 relates to the invention of claim 1, in which the solid organic conductive material is an organic semiconductor, and more specifically the organic semiconductor is composed of 7,7,8,8-tetracyanoquinodimethane complex and its derivative (hereinafter called TCNQ complexes), and in this constitution, therefore, by dissolving and impregnating TCNQ complexes, the inside of pits of the anode processed by etching can be filled sufficiently with a layer of solid organic conductive material having a high conductivity, and an electrolytic capacitor excellent in impedance characteristic particularly in high frequency region of 100 kHz or more is obtained. Moreover, using a capacitor element prepared by applying TCNQ complexes directly on the separator base material or winding an anode foil and a cathode foil through a separator base material, or a capacitor element laminating one set or two or more sets of anode and cathode by way of a separator base material, by impregnating in the heated and fused solution of TCNQ complexes and cooling and solidifying, the conductivity can be expressed easily, so that an electrolytic capacitor excellent in impedance characteristic can be obtained easily.

[0012]

The invention as set forth in claims 4 to 6 relates to the invention of claim 2, in which the conductive high polymer is a polymer of pyrrole, aniline, thiophen, ethylene dioxythiophen, sulfonated aniline, sulfonated pyrrole, sulfonated thiophen, sulfonated ethylene dioxythiophen, and their derivative polymers (hereinafter they are called polymerizable monomers) (claim 4), or the polymer forming method is a method by liquid phase chemical polymerization, a method by vapor phase polymerization, a method by liquid phase electrolytic polymerization, or a method by making use of residual dry polymer of soluble polymer solution (claim 5), and further the conductive high polymer obtained as a result is chemically polymerized polypyrrole, polyethylene dioxythiophen, and polyaniline, electrolytically polymerized polypyrrole, polyethylene dioxythiophen, and polyaniline, or dry residue sulfonated polyaniline obtained by drying soluble polyaniline derivative solution (claim 6). In this constitution, the inside of pits of the anode processed by etching can be filled sufficiently with a layer of solid organic conductive material having a high conductivity, by immersing and polymerizing the capacitor element in a solution containing at least the polymerizable monomer and a proper oxidizing agent in the case of liquid phase polymerization, by immersing, energizing and polymerizing the capacitor element in a solution containing at

least the polymerizable monomer and a proper oxidizing agent in the case of electrolytic polymerization, or by immersing the capacitor element in a solution containing at least a proper oxidizing agent (or immersing and then lifting and drying), and then placing the capacitor element in the vapor phase containing at least the polymerizable monomer in the case of vapor phase polymerization, so that an electrolytic capacitor excellent in impedance characteristic particularly in high frequency region of 100 kHz or more is obtained. Further, by direct vapor phase polymerization of the conductive high polymer on the separator base material, anode or cathode, the conductivity is easily expressed, so that an electrolytic capacity excellent in impedance characteristic may be obtained easily.

[0013]

Further, since these conductive high polymers have a high compatibility in an electrolyte solution composed mainly of an organic matter, when impregnated with the electrolyte solution, it is quickly swollen and diffused into the inner parts of the conductive high polymer, and when composing a capacitor element having the dielectric oxide film coated with conductive high polymer, the capacity for restoring the dielectric oxide film can be maintained at high level.

[0014]

The invention as set forth in claim 7 relates to the invention of any one of claims 1 to 6, in which the driving

electrolyte solution is prepared by dissolving an organic acid salt and an inorganic acid salt in a organic solvent capable of swelling by immersing in a solid organic conductive material. In this constitution, as mentioned above, the electrolyte solution quickly swells and diffuses into the inner part of the conductive high polymer, and therefore, when composing a capacitor element having the dielectric oxide film coated with conductive high polymer, the capacity for restoring the dielectric oxide film can be maintained at high level.

[0015]

The invention as set forth in claim 8 relates to the invention of claim 7, in which the electrolyte to be dissolved in the driving electrolyte solution has a concentration of 1 wt.% of the base or hydroxide of the base in the base for composing the electrolyte, and a hydrogen ion concentration of 1.0×10^{-13} mol/dm^3 or more in an aqueous solution of the base or hydroxide of the base at the measuring temperature of 30°C, and as its specific example, as the base for composing the electrolytic, at least one is used as being selected from the group consisting of compound having alkyl substituent amidine group, quaternary salt of compound having alkyl substituent amidine group, tertiary amine and ammonium. In this constitution, leak of electrolyte solution is prevented, and a capacitor of enhanced reliability is obtained.

[0016]

When composing a capacitor of the invention by using an electrolyte solution composed of an electrolyte of a base of a strong basicity of which hydrogen ion concentration is less than 1.0×10^{-13} mol/dm^3 (for example, tetra-alkyl ammonium or tetra-alkyl phosphonium), in long-term environmental test in the compound environments of high temperature and high humidity (for example, 60°C and 95% RH), the sealing member is likely to be damaged by the effects of the base of strong basicity, and leak is likely to occur, and the reliability is slightly inferior.

[0017]

The invention as set forth in claim 9 relates to the invention of claim 8, in which the base for composing the electrolyte is at least one or more selected from the group consisting of a compound having alkyl subsistent amidine group, quaternary salt of compound having alkyl substituent amidine group, tertiary amine, and ammonium, and in these electrolytic substances, when the concentration of the base or hydroxide of base is 1 wt.% and the measuring temperature is 30°C, the hydrogen ion concentration in aqueous solution of base or hydroxide of base is 1.0×10^{-13} mol/dm^3 or more, and therefore the leak due to such strong acidity as mentioned above is less likely to occur.

[0018]

The invention as set forth in claim 10 relates to the

invention of claim 9, in which the quaternary salt of compound having alkyl subsistent amidine group is at least one or more selected from the group consisting of imidazole compound, benzoimidazole compound, and alicyclic amidine compound, being rendered quaternary by alkyl group or aryl alkyl group with 1 to 11 carbon atoms. In this constitution, when hydroxide ions are formed by electrolytic reaction in the electrolyte solution, since the reaction between hydroxide ion and amidine group of N-C-N or reaction of decomposition and ring opening is fast, the electrolytic products disappear quickly, and as a result, even in the condition of high temperature and high humidity, leak of electrolyte solution to outside can be prevented.

[0019]

The invention as set forth in claim 11 relates to the invention of claim 10, in which the quaternary salt of compound having alkyl subsistent amidine group is at least one or more selected from the group consisting of 1-methyl-1,8-diazabicyclo [5,4,0] undecene-7, 1-methyl-1,5-diazabicyclo [4,3,0] nonene-5, 1,2,3-trimethyl imidazolinium, 1,2,3,4-tetramethyl imidazolinium, 1,2-dimethyl-3-ethyl-imidazolinium, 1,3,4-trimethyl-2-ethyl imidazolinium, 1,3-dimethyl-2-heptyl imidazolinium, 1,3-dimethyl-2-(-3' heptyl) imidazolinium, 1,3-dimethyl-2-dodecyl imidazolinium, 1,2,3-trimethyl-1,4,5,6-tetrahydropyrimidium, 1,3-dimethyl imidazolium, 1-methyl-3-ethyl-imidazolium, and 1,3-dimethyl

benzoimidazolium. In this constitution, the conductivity of the electrolyte solution can be heightened and an excellent heat resistance is realized, and therefore, external leak of electrolyte solution at high temperature and high humidity is prevented, and an electrolytic capacitor having an excellent high temperature stability and low impedance is obtained.

[0020]

The invention as set forth in claim 12 relates to the invention of claim 11, in which the boiling point of the solvent of the driving electrolyte solution is 200°C or more, the electric conductivity of the driving electrolyte solution at measuring temperature of 30°C is 1.0 mS/cm or more, and the spark ignition voltage is 80 V or more. In this constitution, it is effective to prevent the problem of electrolytic capacitor for surface mounting, that is, deformation of appearance due to elevation of capacitor internal pressure caused by heat treatment during surface mounting (both capacitor and substrate exposed to high temperature of soldering), and moreover, since the boiling point of the solvent of the electrolyte solution is high (vapor pressure is low), defective soldering when mounting is less likely to occur, and further since the conductivity is high, the impedance performance is maintained, and still more, since the spark ignition voltage is sufficiently high, an electrolytic capacitor having a high dielectric strength is obtained.

[0021]

In the solid electrolytic capacitor for surface mounting having the sealing member composed by using an elastic rubber, the adsorbed moisture contained in the electrode foil of capacitor element, separator, solid electrolytic substance and rubber sealing member, or the adsorbed moisture bonded to the inside of the case is evaporated at once at high temperature at the time of surface mounting, and as a result, the pressure elevation inside the capacitor is extreme, which may lead to defective air tightness of the capacitor or scattering of sealing member, but by containing the electrolyte solution using a solvent of high boiling point (low vapor pressure), the total pressure inside the capacitor can be lowered at the time of mounting. Therefore, by containing the liquid component (herein an electrolyte solution) in addition to the electrolytic substance of solid electrolytic substance type, pressure elevation inside the capacitor can be suppressed, and defective soldering and others can be improved.

[0022]

Examples of solvent of electrolyte having a boiling point of 200°C or more include 3-alkyl-1,3-oxazolidine-2-one (more specifically, 3-methyl-1,3-oxazolidine-2-one: boiling point 260°C), 1,3-dialkyl-2-imidazolidinone other than 1,3-dimethyl-2-imidazolidinone (more specifically, 1,3-dimethyl-2-imidazolidinone: boiling point 236°C, 1,3-

dipropyl-2-imidazolidinone: boiling point 255°C, 1-methyl-3-ethyl-2-imidazolidinone: boiling point 230°C), 1,3,4-trialkyl-2-imidazolidinone (more specifically, 1,3,4-trimethyl-2-imidazolidinone: boiling point 241°C), 1,3,4,5-tetra-alkyl-2-imidazolidinone (more specifically, 1,3,4,5-tetramethyl-2-imidazolidinone: boiling point 249°C), cyclic lactone (more specifically, γ-butyrolactone: boiling point 204°C), polyhydric alcohol (more specifically, ethylene glycol: boiling point 201°C, glycerin: boiling point 290°C), carbonate (more specifically, ethylene carbonate: boiling point 238°C, propylene carbonate: 242°C), and others.

[0023]

Hereinafter, preferred embodiments of the invention and prior arts as comparative examples are described below while referring to the attached drawings.

[0024]

Fig. 1 (a) and Fig. 1 (b) are a partial sectional perspective view showing a constitution of an electrolytic capacitor of the invention, and a conceptual view magnifying essential parts of its element, and in Fig. 1 (b), the surface is roughened by etching process, and then a dielectric oxide film 11 is formed by oxidation treatment, an anode foil 1 composed of an aluminum foil forming a solid organic conductive material 2 on its surface, and a cathode foil 3 formed by etching an aluminum foil are wound around a separator 4, or, after roughening the surface by etching

process, an anode foil 1 composed of an aluminum foil forming a dielectric oxide film 11 by oxidation treatment and a cathode foil 3 formed by etching process of aluminum foil are wound through an electrolytic paper 4A, then by high temperature treatment thereof, the electrolytic paper 4A is treated by any method of carbonization treatment, and a capacitor element 12 or 12A is formed, between the dielectric oxide film 11 and cathode foil 3, a solid organic conductive material 2 is formed. It is impregnated with an electrolyte 10, and swollen and infiltrated into the solid organic conductive material 2, and thus, the capacitor element 12 or 12A is composed. The capacitor element 12 or 12A is put in a cylindrical aluminum metallic case 8 with a bottom as shown in Fig. 1 (a), further, the releasing end of the aluminum metallic case 8 is sealed so that a sealing member 7 made of rubber may penetrate through an anode lead 5 and a cathode lead 6 for external lead-out being led out from the anode foil 1 and cathode foil 3 from the sealing member 7, and thus, the side surface of the metallic case 8 is covered with an external tube 9.

[0025]

Fig. 2 (a) to Fig. 2 (g) show the manufacturing process for manufacturing the anode foil 1 for electrolytic capacitor of the invention in batch, first as shown in Fig. 2 (a), an etching foil 22 (Fig. 2 (b)) obtained by etching an aluminum foil 21 is oxidized, and an anode foil 1 forming a dielectric oxide film

11 is formed (Fig. 2 (c)). Successively, this anode foil 1 is impregnated in a solution 23 containing a polymerizable monomer capable of forming a conductive high polymer layer as shown in Fig. 2 (d), and lifted, then heated (also dried) by a heating oven 24 as shown in Fig. 2 (e), and thus, as shown in Fig. 2 (f), an anode foil 1 forming a solid organic conductive material 2 on the surface is composed. Next, as shown in Fig. 2 (g), thus constituted anode foil 1 and the cathode foil 3 formed by etching the aluminum foil 21 are wound through a separator 4, and a capacitor element 12 is composed. The subsequent process is same as in the above manufacturing method, and the capacitor element 12 is put into a cylindrical metallic case 8 with a bottom together with electrolyte solution 10, and the releasing end of the metallic case 8 is sealed, by using a sealing member 7, so that an anode lead 5 and a cathode lead 6 for external lead-out being led out from the anode foil 1 and cathode foil 3 respectively may penetrate through the sealing member 7, and thereby the side of the metallic case 8 is covered with an external tube 9.

[0026]

The electrolyte solution used in the electrolytic capacitor of the invention is specifically described below.

As the solvent for the electrolyte solution of the electrolytic capacitor of the invention, an organic solvent stable electrically and chemically and capable of swelling in

the organic conductive material is used, preferably mainly composed of γ-butyrolactone and/or ethylene glycol (both desired to have a boiling point of 200°C or more). In addition, for the purpose of improving the low temperature characteristic and enhancing the dielectric strength, other organic solvent compatible with γ-butyrolactone and/or ethylene glycol may be mixed as a subsidiary solvent, but the subsidiary solvent is not required to be an organic solvent capable of swelling in an organic conductive material.

[0027]

As the subsidiary solvent, in addition to the organic solvent with boiling point of 200°C or more mentioned above, the following organic solvents may be used either alone or as a mixed solvent of two or more kinds, that is, polyhydric alcohol system solvents (propylene glycol, diethylene glycol, 1,4-butane diol, polyoxy alkylene polyol), lactone system solvents (γ-valerolactone, δ-valerolactone, 3-ethyl-1,3-oxyzolidine-2-one), water, amide system solvents (N-methyl formamide, N,N-dimethyl formamide, N-methyl acetamide), ether system solvents (methylal, 1,2-dimethoxy ethane, 1-ethoxy-2-methoxy ethane, 1,2-diethoxy ethane), nitrile system solvents (acetonitrile, 3-methoxy propionitrile), furane system solvents (2,5-dimethoxy tetrahydrofurane), 2-imidazolidinone system solvents (1,3-dimethyl-2-imidazolidinone), and others.

[0028]

In the case of mixed solvent, the mixing ratio of the solvent is preferred to be 40 parts by weight of a solvent of which boiling point is less than 200°C in 100 parts by weight of solvent of which boiling point is 200°C or more. If the content of the solvent of which boiling point is less than 200°C is more than 40 parts, the heat resistance is lowered when an electrolytic capacitor is formed for surface mounting, and the defective rate of soldering becomes higher.

[0029]

Examples of tertiary amine used in the electrolyte of the invention include trialkylamines (trimethylamine, dimethylethylamine, methyldiethylamine, triethylamine, dimethyl n-propylamine, dimethyl isopropylamine, methyl ethyl n-propylamine, methylethyl isopropylamine, diethyl n-propylamine, diethyl isopropylamine, tri-n-propylamine, tri-isopropylamine, tri-n-butylamine, tri-tert-butylamine, etc.), and phenyl group containing amines (dimethyl phenylamine, methylethyl phenylamine, diethyl phenylamine, etc.).

[0030]

Among them, trialkylamine having a high conductivity is preferred. More preferably, it is preferred to use at least one selected from the group consisting of trimethylamine, dimethylethylamine, methyl diethylamine, and triethylamine, and by the use thereof, a capacitor high in conductivity and having an excellent impedance performance is obtained.

[0031]

Examples of compound having alkyl substituent amidine group used in the electrolyte solution of the invention include imidazole compound, benzoimidazole compound, and alicyclic amidine compound (pyrimidine compound, imidazoline compound). More specifically, it is preferred to use 1,8-diazabicyclo [5,4,0] undecene-7, 1,5-diazabicyclo [4,3,0] nonene-5, 1,2-dimethyl imidazolinium, 1,2,4-trimethyl imidazoline, 1-methyl-2-ethyl-imidazoline, 1,4-dimethyl-2-ethyl imidazoline, 1-methyl-2-heptyl imidazoline, 1-methyl-2-(3' heptyl) imidazoline, 1-methyl-2-dodecyl imidazoline, 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine, 1-methyl imidazole, and 1-methyl benzoimidazole, and when these compounds are used, a capacitor having a high conductivity and excellent impedance performance is obtained.

[0032]

In the examples of quaternary salt of compound having alkyl substituent amidine group used as the electrolyte solution is preferred to be a quaternary compound formed by alkyl group or aryl alkyl group with 1 to 11 carbon atoms is preferred, and preferred examples of amidine group are imidazole compound, benzoimidazole compound, and alicyclic amidine compounds (pyrimidine compound, imidazoline compound). Specific preferred examples include 1-methyl-1,8-diazabicyclo [5,4,0] undecene-7, 1-methyl-1,5-diazabicyclo [4,3,0] nonene-5,

1,2,3-trimethyl imidazolinium, 1,2,3,4-tetramethyl imidazolinium, 1,2-dimethyl-3-ethyl-imidazolinium, 1,3,4-trimethyl-2-ethyl imidazolinium, 1,3-dimethyl-2-heptyl imidazolinium, 1,3-dimethyl-2-(-3' heptyl) imidazolinium, 1,3-dimethyl-2-dodecyl imidazolinium, 1,2,3-trimethyl-1,4,5,6-tetrahydropyrimidium, 1,3-dimethyl imidazolium, 1-methyl-3-ethyl-imidazolium, and 1,3-dimethyl benzoimidazolium, and by using these compounds, it is possible to obtain an electrolytic capacitor with an excellent long-term stability having a high heat resistance, high conductivity, and excellent impedance performance.

[0033]

Examples of organic acid used in the electrolyte solution of the invention include the following compounds: polycarboxylic acid (valence of 2 to 4), aliphatic polycarboxylic acid (saturated polycarboxylic acid, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebatic acid, 1,6-decanoic dicarboxylic acid, 5,6-decanoic dicarboxylic acid, 1,7-octanoic dicarboxylic acid, and unsaturated polycarboxylic acid, for example, maleic acid, fumaric acid, itaconic acid, aromatic polycarboxylic acid (for example, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid), alicyclic polycarboxylic acid (for example, cyclohexane-1,2-

dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, etc.), hexahydrophthalic acid, alkyl substituents with 1 to 3 carbon atoms of their polycarboxylic acids (for example, citraconic acid, dimethyl maleic acid), or nitro substitutes (nitrophthalic acid, 3-nitrophthalic acid, 4-nitrophthalic acid), and polycarboxylic acid containing sulfur (for example, thiopropionic acid), monocarboxylic acid, aliphatic monocarboxylic acid with 1 to 30 carbon atoms (for example, formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, perargonic acid, lauric acid, mystyric acid, stearic acid, behenic acid, other saturated carboxylic acid, and acrylic acid, methacrylic acid, oleic acid, and other unsaturated carboxylic acid), aromatic monocarboxylic acid (for example, benzoic acid, o-nitrobenzoic acid, p-nitrobenzoic acid, cinnamic acid, naphthoic acid), and oxycarboxylic acid (for example, salicylic acid, mandelic acid, resorcylic acid). Among these compounds, particularly preferred compounds are those having high conductivity and excellent thermal conductivity such as maleic acid, phthalic acid, cyclohexane carboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, adipic acid, and benzoic acid.

[0034]

The ratio of organic acid and base for composing the

electrolyte solution is usually 4 to 11 at the pH of the electrolyte, and preferably 6 to 9. Out of this range, the spark voltage of the electrolyte solution (dielectric strength) is lowered.

[0035]

As the electrolytic salt, organic carboxylic acids stable electrically and chemically are desired. Preferred examples of such organic carboxylic acid include maleic acid, phthalic acid, cyclohexane carboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, adipic acid, and quaternary salt of compound having alkyl substituent amidine group of benzoic acid.

[0036]

The electrolyte solution of the electrolytic capacitor of the invention may mix and contain various additives as required. Usable additives include phosphor compounds (phosphoric acid, ester phosphate, etc.),complex compound with boric acid compounds [(boric acid, complex of boric acid and polysaccharides (mannite, sorbit, etc.), boric acid and polyhydric alcohol (ethylene glycol, glycerin, etc.)], nitro compounds (o-nitrobenzoic acid, n-nitrobenzoic acid, p-nitrobenzoic acid, o-nitrophenol, m-nitrophenol, p-nitrophenol, p-nitroacetophenone, etc.), and others. In the aluminum electrolytic capacitor, mixing of these additives will improve the restoration of aluminum oxide film. As a result,

it is preferred because an electrolytic capacitor of high dielectric strength can be formed easily.

[0037]

As the bar element for the terminal of the electrolytic capacitor of the invention, a material undergoing corrosion preventive treatment may be used. By corrosion preventive treatment of the bar element, electrolytic current can be suppressed, and the sealing performance may be enhanced. Corrosion preventive treatment of the bar element is preferred to be done on both terminals of anode and cathode, but only either one may be treated. As means of corrosion preventive treatment, anode oxidation treatment in aqueous solution, coating-sintering of metal alkoxide, and coating-sintering of colloidal solution of metal oxide (colloidal solution of silicon dioxide and titanium dioxide) are convenient and preferred.

[0038]

The sealing member 7 is preferably an elastic material mainly composed of rubber polymer formed of a copolymer of isobutylene, isoprene and divinyl benzene, comprising 0.5 to 20 parts of vulcanizing agent such as peroxide or alkyl phenol formalin resin. In other vulcanizing method using other vulcanizing agent than peroxide or alkyl phenol formalin resin (for example, sulfur vulcanization), the rubber elasticity drops significantly when left over for a long period in the condition of high temperature and high humidity, and sufficient

sealing performance is not obtained, and as a result the organic conductive material may oxidize and deteriorate due to invasion of water from outside.

[0039]

Preferred embodiments of the invention are described below. In the embodiments, a "part" always refers to a "part by weight."

[0040]

The composition of the electrolyte solutions used in the preferred embodiments of the invention and in comparative examples is as follows. As the index of hydrogen ion concentration of the base of the electrolyte or the hydroxide of the base in an aqueous solution, the pH is expressed as a note. The pH is defined in the formula: pH = -log [hydrogen ion concentration]. Therefore, if the pH is 13 or less, it means that the hydrogen ion concentration is 1.0×10^{-13} mol/dm^3 or more. Besides, an aluminum foil having a dielectric oxide film formed on the surface at voltage of 500 V was immersed in the electrolyte (temperature 30°C). In this state, the spark ignition voltage of electrolyte solution (that is, the dielectric strength of electrolyte solution) observed by constant voltage-current elevation at constant current of 2.0 mA/cm^2 and the conductivity (measuring temperature 30°C) are shown.

[0041]

Electrolyte solution A

γ-butyrolactone (100 parts), mono-1,2,3,4-tetramethyl

imidazolinium phthalate (30 parts) [note: pH = 11.2], o-nitrobenzoic acid (1 part), monobutyl ester phosphate (1 part), boric acid (2 parts), and mannite (2 parts) were mixed and dissolved.

The spark voltage was 85 V, and the conductivity was 9.0 mS/cm.

[0042]

Electrolyte solution B

γ-butyrolactone (50 parts), ethylene glycol (50 parts), trimethyl ammonium maleate (5 parts) [note: pH = 9.5], trimethylamine phthalate (5 parts) [note: pH = 9.5], diammonium adipate (3 parts) [note: pH = 9.1], boric acid (0.5 part), p-nitrobenzoic acid (1 part), and phosphoric acid (0.5 part) were mixed and dissolved.

The spark voltage was 180 V, and the conductivity was 3.3 mS/cm.

[0043]

Electrolyte solution C

Ethylene glycol (70 parts), glycerin (30 pats), diammonium adipate (15 parts) [note: pH = 9.1], 1,6-decane dicarboxylic acid (1 part) [note: pH = 9.1], 1,7-octane dicarboxylic acid (1 part) (note: pH = 9.1], o-nitrophenol (1 part), and ammonium hypophosphite (1 part) [note: pH = 9.1] were mixed and dissolved.

The spark voltage was 340 V, and the conductivity was 0.9 mS/cm.

[0044]

Electrolyte solution D:

γ-butyrolactone (100 parts) and tetramethyl ammonium phthalate (40 parts) [note: pH = 13.2] were mixed and dissolved.

The spark voltage was 79 V, and the conductivity was 11.5 mS/cm.

[0045]

The sealing members of rubber used in the preferred embodiments of the invention and comparative examples are as follows.

[0046]

Sealing member A [vulcanization by peroxide]

It was vulcanized and formed by mixing 30 parts of rubber polymer composed of a copolymer of isobutylene, isoprene and divinyl benzene, 20 parts of carbon, 50 parts of inorganic filler, and 2 parts of dicumyl peroxide as a vulcanizing agent. The hardness of the sealing member after forming was measured on the surface portion at the side contacting with the capacitor element between two rubber holes for penetrating a lead, and the surface of the portion contacting with the lead wire side of the rubber hole inside. As a result, the IRHD (international rubber hardness degree) was respectively 67 IRHD and 66 IRHD.

[0047]

Sealing member B [vulcanization by resin]

It was vulcanized and formed by mixing 30 parts of rubber

polymer composed of a copolymer of isobutylene and isoprene, 20 parts of carbon, 50 pats of inorganic filler, and 2 parts of alkyl phenol formalin resin as vulcanizing agent. The hardness of the sealing member after forming was measured on the surface portion at the side contacting with the capacitor element between two rubber holes for penetrating a lead, and the surface of the portion contacting with the lead wire side of the rubber hole inside. As a result, the IRHD (international rubber hardness degree) was respectively 77 IRHD and 76 IRHD.

[0048]

(Preferred Embodiment 1)

An anode aluminum foil and a cathode aluminum foil were wound around an electrolytic paper containing Manila hemp fibers (density 0.55 g/cm^3, thickness 50 μm). Thus prepared winding type aluminum electrolytic capacitor was kept at temperature of 300°C for 30 minutes, and the electrolytic paper was carbonized. Then, this capacitor element was immersed in a water-ethanol solution containing ethylene dioxythiophen and ferric sulfate, and lifted, and polymerized (10 minutes at 105°C), and this process was repeated 10 times. The solid organic conductive material layer composed of polyethylene dioxythiophen thus polymerized chemically was formed on the electrode foils and between electrode foils. Consequently, the capacitor element was washed in water, and dried. Further, electrolyte A was impregnated in this capacitor element. As

a result, an aluminum electrolytic capacitor element with rated voltage of 50 V and electrostatic capacity of 390 μF was obtained. This capacitor element was put in an aluminum metallic case together with sealing member A, and the opening was sealed by curling process. Thus, an aluminum electrolytic capacitor was composed (size: ϕ13 mm×L 20 mm).

[0049]

(Preferred Embodiment 2)

A glass fiber nonwoven cloth (density 0.13 g/cm^3, thickness 50 μm), an anode aluminum foil, and a cathode aluminum foil were immersed in a water-ethanol solution containing pyrrole and ammonium persulfate, and lifted, dried and polymerized (10 minutes at 105°C), and this process was repeated three times. Thus, a chemically polymerized polypyrrole was formed. Then, washing in water and drying, the separator made conductive by the chemically polymerized polypyrrole, and the anode aluminum foil and cathode aluminum foil having the chemically polymerized polypyrrole formed on the surface were obtained. Then, through this conductive separator, the anode aluminum foil and cathode aluminum foil having the chemically polymerized polypyrrole formed on the surface were wound, and a capacitor element was formed. It was further immersed in soluble sulfonated polyaniline solution at concentration of 10 wt.%, impregnated at reduced pressure, lifted, and dried. Thus, the residual dried sulfonated polyaniline was formed between

the anode aluminum foil and cathode aluminum foil having chemically polymerized polypyrrole. Thus, the electric bonding between the electrode foils was reinforced. Still more, this capacitor element was impregnated in electrolyte A. As a result, an aluminum electrolytic capacitor element with rated voltage of 50 V and electrostatic capacity of 390 μF was obtained. This capacitor element was put in an aluminum metallic case together with sealing member A, and the opening was sealed by curling process. Thus, an aluminum electrolytic capacitor was composed (size: ϕ13 mm×L 20 mm).

[0050]

(Preferred Embodiment 3)

On a glass fiber nonwoven cloth (density 0.13 g/cm^3, thickness 50 μm), an anode aluminum foil, and a cathode aluminum foil, 7,7,8,8-tetracyanoquinodimethane complex in molten state was applied individually. Then, by cooling, the separator made conductive by the 7,7,8,8-tetracyanoquinodimethane complex, and the anode aluminum foil and cathode aluminum foil having the 7,7,8,8-tetracyanoquinodimethane complex formed on the surface were obtained. Then, through this conductive separator, the anode aluminum foil and cathode aluminum foil having the 7,7,8,8-tetracyanoquinodimethane complex formed on the surface were wound. Thus a capacitor element was formed. It was further immersed in soluble sulfonated polyaniline solution at concentration of 10 wt.%, impregnated at reduced pressure,

lifted, and dried at a temperature below the melting point of the 7,7,8,8-tetracyanoquinodimethane complex. Thus, the residual dried sulfonated polyaniline was formed between the anode aluminum foil and cathode aluminum foil having the 7,7,8,8-tetracyanoquinodimethane complex. Thus, the electric bonding between the electrode foils was reinforced. Still more, this capacitor element was impregnated in electrolyte A. As a result, an aluminum electrolytic capacitor element with rated voltage of 50 V and electrostatic capacity of 390 μF was obtained. This capacitor element was put in an aluminum metallic case together with sealing member A, and the opening was sealed by curling process. Thus, an aluminum electrolytic capacitor was composed (size: ϕ13 mm×L 20 mm).

[0051]

(Preferred Embodiment 4)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that electrolyte solution B was used as the electrolyte solution in preferred embodiment 1 of the invention.

[0052]

(Preferred Embodiment 5)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that electrolyte solution C was used as the electrolyte solution in preferred embodiment 1 of the invention.

[0053]

(Preferred Embodiment 6)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that electrolyte solution D was used as the electrolyte solution in preferred embodiment 1 of the invention.

[0054]

(Preferred Embodiment 7)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that sealing member B was used as the sealing member in preferred embodiment 1 of the invention.

[0055]

(Preferred Embodiment 8)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that pyrrole was used instead of ethylene dioxythiophen in preferred embodiment 1 of the invention.

[0056]

(Preferred Embodiment 9)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that aniline was used instead of ethylene dioxythiophen in preferred embodiment 1 of the invention.

[0057]

(Preferred Embodiment 10)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that a mixture of iron p-toluene sulfonate and iron dodecyl benzene sulfonate was used instead of ferric sulfate, and that water-methanol solution was used instead of water-ethanol solution in preferred embodiment 1 of the invention.

[0058]

(Preferred Embodiment 11)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that a mixture of ammonium persulfate and hydrogen persulfate water was used instead of ferric sulfate in preferred embodiment 1 of the invention.

[0059]

(Comparative Example 1)

An anode aluminum foil and a cathode aluminum foil were wound around an electrolytic paper containing Manila hemp fibers (density 0.55 g/cm^3, thickness 50 μm). Thus a capacitor element was prepared. This capacitor element was impregnated in electrolyte solution A, and an aluminum electrolytic capacitor element with rated voltage of 50 V and electrostatic capacity of 390 μF was obtained. This capacitor element was put in an aluminum metallic case together with sealing member A. Then the opening was sealed by curling process. Thus, an aluminum electrolytic capacitor was composed (size: ϕ13 mm×L 20 mm).

[0060]

(Comparative Example 2)

An electrolytic capacitor was prepared in the same manner as in preferred embodiment 1 except that electrolyte solution A was not impregnated in preferred embodiment 1 of the invention.

[0061]

(Comparative Example 3)

An anode aluminum foil and a cathode aluminum foil were wound around an electrolytic paper containing Manila hemp fibers (density 0.55 g/cm^3, thickness 50 μm). Thus a capacitor element was prepared. This capacitor element was kept at temperature of 300°C for 30 minutes, and the electrolytic paper was carbonized. Then this element was immersed in 7,7,8,8-tetracyanoquinodimethane complex in molten state and impregnated at reduced pressure. By cooling, a 7,7,8,8-tetracyanoquinodimethane complex layer was formed directly between the electrodes. Thus, an aluminum electrolytic capacitor element with rated voltage of 50 V and electrostatic capacity of 390 μF was obtained. This capacitor element was put in an aluminum metallic case together with sealing member A, and the opening was sealed by curling process. Thus, an aluminum electrolytic capacitor was composed (size: ϕ13 mm× L 20 mm).

[0062]

(Comparative Example 4)

An anode aluminum foil and a cathode aluminum foil were wound around a glass fiber nonwoven cloth (density 0.13 g/cm^3, thickness 50 μm), and the obtained aluminum electrolytic capacitor element was immersed in an aqueous solution of manganese nitrate, lifted, and pyrolyzed (10 minutes at 300°C), and this process was repeated 10 times, and a manganese dioxide layer which is a solid inorganic conductive material was directly formed between the electrodes. This capacitor element was impregnated in electrolyte solution A. Thus, an aluminum electrolytic capacitor element with rated voltage of 50 V and electrostatic capacity of 390 μF was obtained. This capacitor element was put in an aluminum metallic case together with sealing member A, and the opening was sealed by curling process. Thus, an aluminum electrolytic capacitor was composed (size: ϕ13 mm×L 20 mm).

[0063]

(Comparative Example 5)

An electrolytic capacitor was prepared in the same manner as in comparative example 1 except that carbon fabric weaving carbon fibers was used instead of the electrolytic paper in comparative example 1.

[0064]

(Comparative Example 6)

An electrolytic capacitor was prepared in the same manner as in comparative example 1 except that glass fiber nonwoven

cloth coated with water dispersion type colloidal graphite was used instead of the electrolytic paper in comparative example 1.

[0065]

Table 1 shows results of comparison of initial characteristics (electrostatic capacity, impedance leak current) and number of shorting troubles during aging process in aluminum electrolytic capacitors in preferred embodiments 1 to 11 of the invention and comparative examples 1 to 6.

[0066]

In each material, the number of samples was 20, and the initial characteristic (except for shorting troubles) is expressed by the average of 20 samples.

[0067]

[Table 1]

	Electrostatic capacity (μF) f=120 Hz	Leak current (μA) at rated voltage, 2 min	Number of shorting troubles during aging	Impedance (mΩ) f=400 kHz
Preferred embodiment 1	390	92	None	10
Preferred embodiment 2	390	90	None	11
Preferred embodiment 3	370	93	None	11
Preferred embodiment 4	393	90	None	12
Preferred embodiment 5	385	88	None	22
Preferred embodiment 6	380	180	None	10
Preferred embodiment 7	390	89	None	11
Preferred embodiment 8	390	89	None	12
Preferred embodiment 9	384	90	None	13
Preferred embodiment 10	360	91	None	13
Preferred embodiment 11	380	91	None	11
Comparative example 1	395	70	None	41
Comparative example 2	360	1000 or more	15 times	15
Comparative example 3	385	1000 or more	18 times	13
Comparative example 4	385	195	2 times	18
Comparative example 5	380	170	None	30
Comparative example 6	390	1000 or more	17 times	25

[0068]

As clear from Table 1, the electrolytic capacitors in preferred embodiments 1 to 11 of the invention is extremely small in impedance as compared with the electrolytic capacitor

composed only of electrolyte solution in comparative example 1.

[0069]

In the aluminum electrolytic capacitor lowered in resistance by using carbon fabric weaving carbon fibers as means of making the separator conductive in comparative example 5, the impedance is improved as compared with comparative example 1, but the impedance is larger than in the electrolytic capacitors in preferred embodiments 1 to 11.

[0070]

In the electrolytic capacitors in the comparative examples, that is, in the aluminum electrolytic capacitor not having electrolyte solution using only conductive high polymer (polyethylene dioxythiophen layer) in comparative example 2, in the aluminum electrolytic capacitor not having electrolyte using only organic semiconductor (7,7,8,8-tetracyanoquinodimethane complex layer) in comparative example 3, and in the aluminum electrolytic capacitor lowered in resistance by applying water dispersion type colloidal graphite as the conductive means of separator in comparative example 6, shorting troubles (shorting between electrodes due to lack of dielectric strength) occurred in all samples during aging process for applying a direct voltage of 63 V at temperature of 85°C.

[0071]

In the aluminum electrolytic capacitor using manganese dioxide which is a solid inorganic conductive material, instead of solid organic conductive material, in comparative example 4, although the impedance is excellent, since the conductive material is inorganic, the electrolyte solution, which is an organic matter, is hardly diffused, and the restoration performance of the dielectric oxide film was not assured sufficiently. Accordingly, slight shorting troubles occurred during aging.

[0072]

As explained herein, the invention presents, in a simple process, electrolytic capacitors having excellent characteristics, such as excellent impedance characteristic, small leak current, superior reliability, and high dielectric strength. Of the preferred embodiments of the invention, in preferred embodiment 6 of the invention using electrolyte solution D, since the spark ignition voltage of electrolyte is below 80 V, the dielectric strength is not sufficient, and the leak current value tends to be higher as compared with other preferred embodiments although shorting did not occur during aging. Therefore, to express the effects of the invention sufficiently in the aspects of dielectric strength and leak current, the spark ignition voltage of the electrolyte is preferred to be 80 V or more.

[0073]

Of the preferred embodiments of the invention, in preferred embodiment 5 of the invention using electrolyte solution C, since the conductivity of the electrolyte solution is less than 1.0 mS/cm, the conductivity is not sufficient, and the impedance tends to be higher as compared with other preferred embodiments. In order to express the effects of the invention sufficiently in the aspect of impedance performance, the conductivity of the electrolyte solution is preferred to be 1.0 mS/cm or more.

[0074]

Table 2 shows the results of observation of the sealing member surface after 1000 hours of continuous application test of rated voltage of 50 V in the atmosphere of temperature of 60°C and relative humidity of 95%, in aluminum electrolytic capacitors in preferred embodiments 1 to 11 of the invention. The number of samples is 20 each.

[0075]

[Table 2]

	Appearance of sealing member surface after 1000 hours of humidity resistance test at 60°C, 95% RH
Preferred embodiment 1	No abnormality
Preferred embodiment 2	No abnormality
Preferred embodiment 3	No abnormality
Preferred embodiment 4	No abnormality
Preferred embodiment 5	No abnormality
Preferred embodiment 6	Electrolyte leak from cathode lead in 2 samples
Preferred embodiment 7	No abnormality
Preferred embodiment 8	No abnormality
Preferred embodiment 9	No abnormality
Preferred embodiment 10	No abnormality
Preferred embodiment 11	No abnormality

[0076]

As clear from Table 2, extreme abnormality was not observed in any preferred embodiment. However, in preferred embodiment 6 using electrolyte solution D, since the base of the electrolytic material is a base of strong basicity with hydrogen ion concentration of less than 1.0×10^{-13} mol/dm^3, in the long-term test in complex environments of high temperature and high humidity, the sealing member (sealing portion) is likely to be damaged by the effects of the base of strong basicity, and, as a result, electrolyte leak was observed in two samples. The electrolyte leaks from the lead. In order to express the effects of the invention sufficiently in the aspect of

reliability, in the base for composing the electrolytic substance, the concentration of the base or the hydroxide of the base is preferred to be 1 wt.% or more, and when the measuring temperature is 30°C, the hydrogen ion concentration of the base or the hydroxide of the base in aqueous solution is preferred to be selected at 1.0×10^{-13} mol/dm^3 or more.

[0077]

According to the method of preferred embodiments 1 to 11 of the invention and comparative examples 2 and 3, again, aluminum electrolytic capacitor elements with rated voltage of 6.3 V and electrostatic capacity of 1000 μF were obtained. This capacitor element was put in a aluminum metallic case together with the sealing member A. Then the opening was sealed by curling process. Consequently, a resin seat plate made of polyphenylene sulfide was mounted. As a result, an aluminum electrolytic capacitor of vertical surface mounting type was fabricated (size: ϕ10 mm×L 10 mm). Thus composed aluminum electrolytic capacitor of surface mounting type was mounted on a glass epoxy substrate (2 mm thick) by using cream solder (Sn-Pb eutectic composition). By passing through a reflow furnace for infrared and hot air treatment (peak temperature 240°C, exposure time to temperature of 200°C or more of 50 seconds), mounting and heat resistance test was conducted. The number of samples was 20.

[0078]

As a result, the surface mounting type aluminum electrolytic capacitors composed in the methods conforming to preferred embodiments 1 to 11 of the invention were suppressed in pressure elevation in the capacitor due to water adsorbed on the members because the electrolyte solution was composed of an organic solvent with boiling point of 200°C or more added to solid organic conductive material as electrolytic substance. Hence, mounting troubles due to scatter of sealing member of swelling of sealing member did not occur. On the other hand, in the surface mounting type aluminum electrolytic capacitors composed in the methods conforming to comparative examples 2 and 3, the pressure elevation in the capacitor due to adsorbed water was extreme, and the sealing members scattered in all 20 samples. Evidently, the surface mounting type aluminum electrolytic capacitors manufactured in the methods of the preferred embodiments of the invention were enhanced in heat resistance when mounting, by using the electrolyte solution composed of organic solvent of boiling point of 200°C or more, in addition to the solid organic conductive material.

[0079]

[Advantage of the Invention]

Thus, the electrolytic capacitors of the invention have excellent characteristics such as excellent impedance characteristic, small leak current, excellent reliability, and high dielectric strength, and hence, its industrial values are

outstanding.

[Brief Description of the Drawings]

Fig. 1 (a) is a partial sectional perspective view showing a configuration of an electrolytic capacitor according to a first preferred embodiment of the invention.

Fig. 1 (b) is a magnified conceptual diagram of essential parts of a capacitor element thereof.

Fig. 2 (a) to (g) are manufacturing process diagrams for manufacturing an anode foil of the electrolytic capacitor of the preferred embodiment.

[Description of the Reference Numerals]

1 Anode foil

2 Solid organic conductive material

3 Cathode foil

5 Anode lead

6 Cathode lead

7 Sealing member

8 Metallic case

9 Outer tube

10 Electrolyte solution

11 Dielectric oxide film

21 Aluminum foil

22 Etching foil

23 Solution containing polymerizable monomer

24 Heating furnace

[Name of the Document] Abstract

[Abstract]

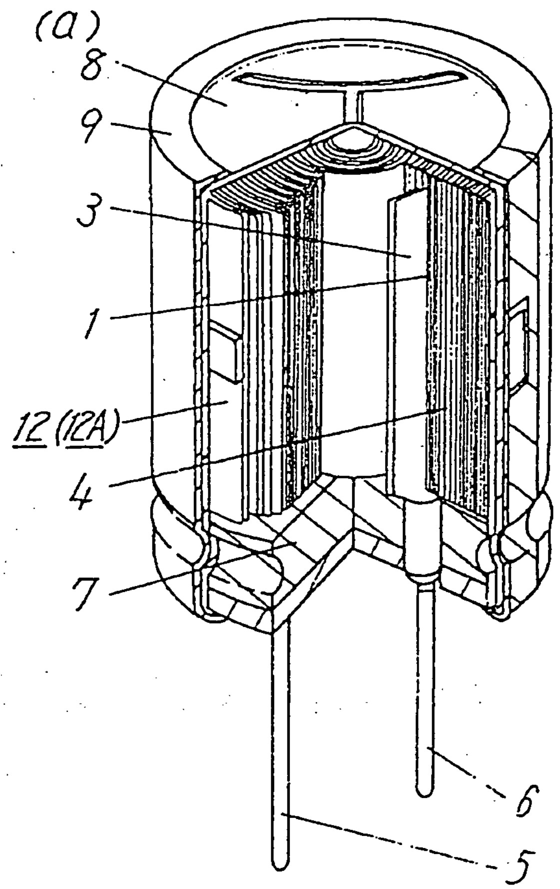
[Object] To obtain an electrolytic capacitor of high dielectric strength excellent in impedance characteristic, leak current, and reliability.

[Means to Solve the Problems] The electrolytic capacitor uses a capacitor element 12 composed of an anode foil 1 formed of a valve action metal having a dielectric oxide film formed on the surface, a cathode foil 3, a solid organic conductive material 2 disposed between the anode foil 1 and cathode foil 3, and a driving electrolyte solution 10, and therefore an electrolytic capacitor of high dielectric strength excellent in impedance characteristic, leak current characteristic, and reliability is realized.

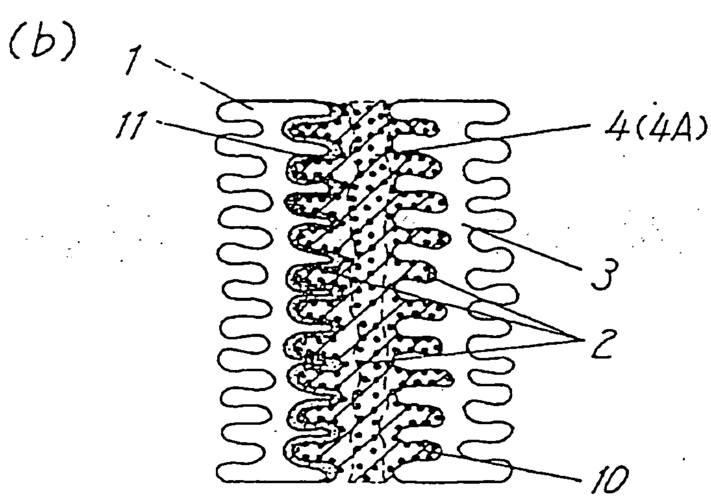
[Selected Drawing] Fig. 1

[Name of the Document] Drawing

[Fig. 1]



1	Anode foil
2	Solid organic conductive material
3	Cathode foil
4	Separator
4A	Carbonized electrolytic paper
5	Anode lead
6	Cathode lead
7	Sealing member
8	Metallic case
9	Outer tube
10	Electrolyte solution
11	Dielectric oxide film
12, 12A	Capacitor element



[Fig. 2]

1 Anode foil
2 Solid organic conductive material
3 Cathode foil
4 Separator
11 Dielectric oxide film
12 Capacitor element
21 Aluminum foil
22 Etching foil
23 Solution co ntaining polymerizable monomer
24 Heating furnace